3-Substituted 1,2,3-Triazole-1-Oxides. Preparation and Reactions
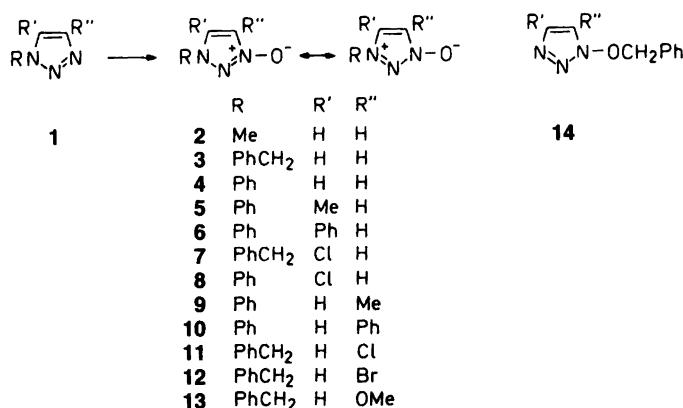
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1-Substituted triazoles and *m*-chloroperoxybenzoic acid produce 3-substituted triazole-1-oxides, activated towards electrophiles, nucleophiles and deprotonation. Thus, the *N*-oxides are alkylated at the *N*-oxygen. They are chlorinated or brominated at C-5. Methoxide ions displace halogen at C-4 readily, and chlorine at C-5 at elevated temperature. Methoxytriazole-1-oxides are demethylated by methoxide ions to hydroxytriazole-1-oxides. Remethylation of these occurs predominantly at the *N*-oxygen, with production of mesoionic *N*-methoxytriazoles. Sodium hydride abstracts H-4 of 3-methyl-5-chlorotriazole-1-oxide. Deprotonation may be followed by addition of electrophiles such as sulfur, dimethyldisulfide or methyl iodide. 3-Methyl-5-bromotriazole-1-oxide abstracts bromonium ions and is debrominated by sodium sulfite. In the presence of sodium methoxide, self-bromination is followed by nucleophilic displacement leading to *cine*-substitution. The triazole-1-oxides can be deoxygenated with phosphorus trichloride. Hence, 3-substituted triazole-1-oxides are excellent precursors for regioselectively substituted triazoles.

3-Substituted benzotriazole-1-oxides are known but no monocyclic 3-substituted triazole-1-oxides have been described. Attempts to oxidize 1-benzyltriazoles with peroxyacetic acid were reported to produce 1-benzyloxytriazoles.[1] We have oxidized a variety of 1-methyl-, 1-benzyl- and 1-phenyltriazoles (**1**) with *m*-chloroperoxybenzoic acid at the more basic N-3 to give the triazole-*N*-oxides **2–13**. We report here the preparation, structure and properties of the 3-substituted triazole-1-oxides **2–13**, which are useful in the synthesis of substituted triazoles.

	R	R'	R"
2	Me	H	H
3	PhCH₂	H	H
4	Ph	H	H
5	Ph	Me	H
6	Ph	Ph	H
7	PhCH₂	Cl	H
8	Ph	Cl	H
9	Ph	H	Me
10	Ph	H	Ph
11	PhCH₂	H	Cl
12	PhCH₂	H	Br
13	PhCH₂	H	OMe

Scheme 1.

Preparation

The compounds prepared are listed in Scheme 1.

The yields of the 3-substituted triazole-1-oxides **2–13** (see Table 1) are good but decrease when electron-attracting substitutents are present, particularly if situated adjacent to the nitrogen atom to be oxidized. Phenyl groups at this position also lead to decreased yields. The low yield in these cases is not a serious drawback since unchanged starting material is easily recovered.

Structure

The structure of the oxidation products **2–13** is apparent from their ready reduction by phosphorus trichloride to the parent triazoles. In the case of **9** and **18**, the structures were proven by X-ray crystallography.[2] Our 3-benzyltriazole-1-oxide (**3**) had the same melting point as that reported for "1-benzyloxytriazole".[1] This observation led us to prepare 1-benzyloxytriazole (**14**) by an independent route, viz. benzylation of 1-hydroxytriazole. The product obtained was an oil, unlike the two possible N-benzyl derivatives, namely 2-benzyltriazole-1-oxide[3] and 3-benzyltriazole-1-oxide (**3**). As expected, it was essentially unaffected by treatment with phosphorus trichloride. Since the previously reported "benzyloxytriazole" is similar to our 3-benzyltriazole-1-oxide (**3**) but dissimilar to our 1-benzyloxytriazole (**14**) it is suggested that all previously reported benzyloxytriazoles[1] are, in fact, 3-benzyltriazole-1-oxides.

Electrophilic addition

The electrophilic addition reactions examined are summarized in Scheme 2.

3-Substituted triazole-1-oxides **2–4** are protonated at the oxygen atom. Thus, hydrochlorides separate from methanolic solutions of **2–4** upon addition of hydrogen chloride in ether solution. The triazole-1-oxides are readily methylated at the N-oxygen atom by trimethyloxonium tetrafluoroborate in liquid sulfur dioxide solution to give stable, but hydroscopic, 1-methoxy 3-substituted triazolium tetrafluoroborates **15–17**. That methylation takes place at the oxygen atom of the triazole-1-oxides is apparent from the low field position (4.4–4.6 ppm) of the ^{1}H NMR signal for the introduced methyl group.
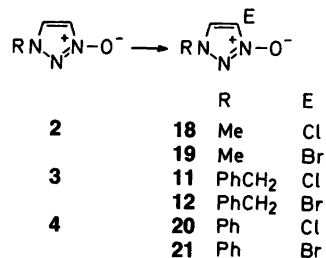

	R
2	**15** Me
3	**16** PhCH$_2$
4	**17** Ph
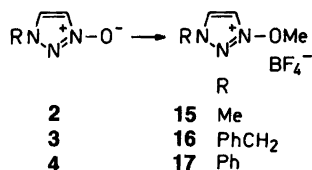
Scheme 2.

Electrophilic substitution

The electrophilic substitution reactions studied are summarized in Scheme 3.

The N-oxygen of pyridine-N-oxides activates the α and γ positions towards electrophilic substitution reactions. The activation is conceivable since reasonable resonance structures with negatively charged α and γ positions can be written. The activation of the 5-position of 2-substituted triazole-1-oxides can likewise be rationalized in terms of a resonance structure with a negatively charged C-5.[4] No reasonable resonance structures with negatively charged ring carbon atoms can be formulated for 3-substituted triazole-1-oxides, nor are the intermediates arising by electrophilic addition to C-4 or C-5 in **2–4** stabilized by the presence of the N-oxygen atom. Therefore, N-oxidation is not expected to activate the triazole nucleus towards electrophiles. However, N-oxidation gives rise to a slight activation. Thus, 1-benzyltriazole (**1**: R=PhCH$_2$, R'=R''=H) is brominated at 20 °C, conversion being complete in 7 d and producing the 4-bromo derivative accompanied by several by-products. Bromination of the corresponding N-oxide **3** requires only 120 h and affords the 5-bromo derivative **12** in quantitative yield. The product is identical with that obtained by oxidation of 1-benzyl-4-bromotriazole (**1**: R=PhCH$_2$, R'=H, R''=Br), proving

		R	E
2	**18**	Me	Cl
	19	Me	Br
3	**11**	PhCH$_2$	Cl
	12	PhCH$_2$	Br
4	**20**	Ph	Cl
	21	Ph	Br

Scheme 3.

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the structure of **12**. The activation was also demonstrated in a competition experiment in which 1 equiv. of 3-benzyltriazole-1-oxide (**3**) and 1 equiv. of the parent triazole (**1**: R=PhCH$_2$, R'=R''=H) were treated with 1-equiv. of bromine. Under these conditions only the *N*-oxide was attacked. All 3-substituted triazole-1-oxides **2–4** were selectively brominated or chlorinated to give the 5-halogeno-substituted derivatives **11**, **12** and **18–21**. On *N*-oxidation N-3 becomes positively charged through resonance. This deactivates the phenyl groups of 3-phenyltriazole-1-oxides which react cleanly without attack of the phenyl group. In contrast, the parent 1-phenyl-triazole (**1**: R=Ph, R'=R''=H) is halogenated at the phenyl group. A complicated mixture arises and trihalogenoaniline can be isolated. The selective halogenation of 3-phenyltriazole-1-oxides (e.g. **4**) followed by deoxygenation with phosphorus trichloride provides a useful route to the otherwise difficultly accessible 1-phenyl-4-halogenotriazoles in high overall yield.
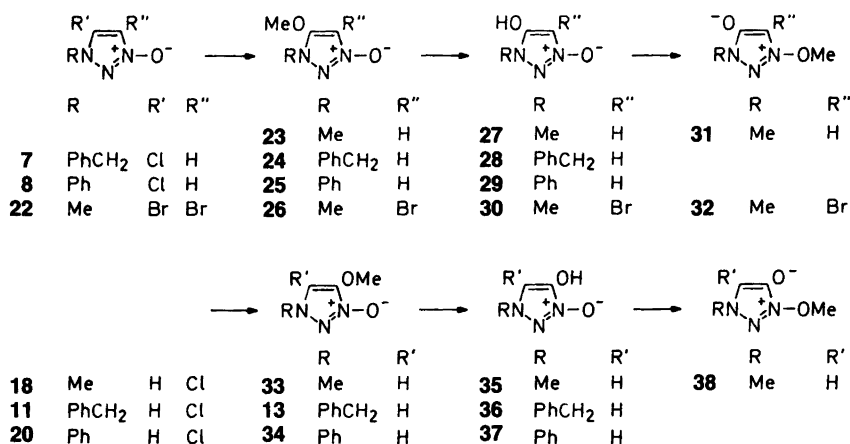
3-Phenyltriazole-1-oxide (**4**) is nitrated selectively at the *para* phenyl position. Presumably, the strong acid protonates the *N*-oxygen atom, thus deactivating the triazolium ring towards further electrophilic attack. Instead, the phenyl group, though deactivated by the positive nitrogen atom, is attacked by the strong electrophile. Nitration can be followed by halogenation and deoxygenation giving rise to 1-*p*-nitrophenyl-4-halogenotriazoles in high yields. The high regioselectivity of electrophilic substitution of

3-substituted triazole-1-oxides may be used advantageously for the preparation of specifically substituted triazoles.

Nucleophilic substitution

The nucleophilic substitution reactions examined are summarized in Scheme 4.

The activation towards nucleophilic displacement reactions of α and γ positions of pyridine-*N*-oxides and of the 5-position of 2-substituted triazole-1-oxides[4] is explained by the existence of resonance structures with a positive charge at these positions. 3-Substituted triazole-1-oxides are devoid of resonance structures with a positive charge at the ring carbon atoms. Nor does the *N*-oxygen contribute to mesomeric stabilization of the intermediates resulting from nucleophilic addition to these positions. However, the negative charge of such adducts may be stabilized inductively by the adjacent nitrogen atoms which become positive on *N*-oxidation. Therefore, *N*-oxidation is expected to activate halogen at both triazole carbon atoms in 3-substituted triazole-1-oxides towards nucleophilic displacement. These predictions proved to be correct. While displacement of the halogen of 1-benzyl-5-chlorotriazole (**1**: R=PhCH$_2$, R'=Cl, R''=H) with methoxide requires heating with 1 M sodium methoxide in methanol at 120°C for 16 h,[5] chlorine in the corresponding *N*-oxide **7** is readily displaced at 20°C. Nucleophilic displacement of halogen in 1-substituted 4-halogenotriazoles has

	R	R'	R''		R	R''		R	R''		R	R''
				23	Me	H	**27**	Me	H	**31**	Me	H
7	PhCH$_2$	Cl	H	**24**	PhCH$_2$	H	**28**	PhCH$_2$	H			
8	Ph	Cl	H	**25**	Ph	H	**29**	Ph	H			
22	Me	Br	Br	**26**	Me	Br	**30**	Me	Br	**32**	Me	Br

	R	R'	R''		R	R'		R	R'		R	R'
					R	R'		R	R'		R	R'
18	Me	H	Cl	**33**	Me	H	**35**	Me	H	**38**	Me	H
11	PhCH$_2$	H	Cl	**13**	PhCH$_2$	H	**36**	PhCH$_2$	H			
20	Ph	H	Cl	**34**	Ph	H	**37**	Ph	H			

Scheme 4.

been attempted[6] but without success. As a control, we heated 1-benzyl-4-chlorotriazole (1: R=PhCH$_2$, R'=H, R''=Cl) with methanolic sodium methoxide at 140°C for 5 h. No conversion was observed. Under similar conditions, the halogen of the corresponding *N*-oxide 11 is displaced quantitatively. The initial product 13 is *O*-dealkylated by methoxide ions at this temperature, producing 3-benzyl-5-hydroxytriazole-1-oxide (36) as the final product. 3-Phenyl-4- and 5-chlorotriazole-1-oxide (8 and 20) reacted analogously, as did 3-methyl-5-chlorotriazole-1-oxide (18).

Both 4- and 5-methoxy-substituted triazole-1-oxides 22, 24, 25, 33, 13 and 34 were demethylated by methoxide ion at elevated temperature to give the corresponding hydroxy-substituted triazole-1-oxides 27, 28, 29, 35, 36 and 37, respectively. The watersoluble 35 was freed from inorganic salts by extraction with pyridine. The water-soluble 27 was prepared using lithium methoxide. During work-up, pyridine was employed to remove the lithium salts (see Experimental).

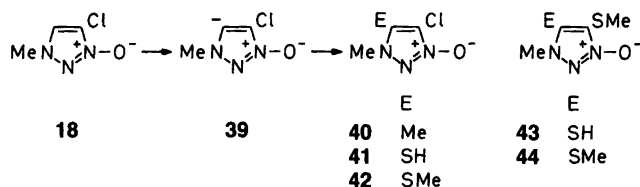Methylation of the hydroxytriazole-1-oxides with methyl iodide took place at both oxygen atoms. Thus, 3-methyl-4-hydroxytriazole-1-oxide (27) produced 6% of 3-methyl-4-methoxytriazole-1-oxide (23) and 85% of the mesoionic *anhydro*-1-methoxy-3-methyl-4-hydroxytriazolium hydroxide (31). Similarly, 3-methyl-5-hydroxytriazole-1-oxide (35) on methylation gave 7% of 3-methyl-5-methoxytriazole-1-oxide (33) and 93% of the mesoionic *anhydro*-1-methoxy-3-methyl-5-hydroxytriazolium hydroxide (38). The mesoionic triazoles 31 and 38 were characterized by a C–O stretching absorption at ca. 1640 cm^{-1} in the IR spectra. This absorption was also observed for *anhydro* 1,3-dialkylhydroxytriazolium hydroxides.[5]

Like the methoxy-substituted triazole-1-oxides, the mesoionic triazoles 31 and 38 are also dealkylated upon heating with 1 M sodium methoxide, re-forming the hydroxy-substituted *N*-oxides 27 and 35, respectively. When the 4,5-di-
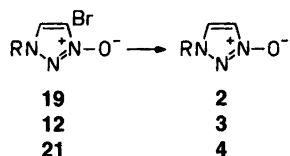
bromo compound 22, prepared as described below, was treated with methanolic sodium methoxide at 20°C only bromine at C-4 was displaced, producing the 4-methoxy-5-bromo compound 26 which is dealkylated by the methoxide ions producing the hydroxy bromo compound 30. Realkylation with methyl iodide yields *anhydro*-1-methoxy-3-methyl-4-hydroxy-5-bromotriazolium hydroxide (32) and 3-methyl-4-methoxy-5-bromotriazole-1-oxide (26) in the ratio 1:2. All nucleophilic displacement reactions indicate high regioselectivity for substitution of halogen at C-4. This is most useful in the synthesis of substituted triazoles and contrasts with the poor regioselectivity attending displacement of 4- and 5-halogen in the corresponding triazolium salts.[7]

Deprotonation

The ring protons of 1-substituted triazoles are not exchanged with deuterium when kept in a solution of sodium methoxide in CH$_3$OD. Abstraction of H-5 of 1-phenyltriazole (1: R=Ph, R'=R''=H) requires butyllithium and leads to ring-cleavage.[8] The ring protons of the corresponding *N*-oxides 2–4 are exchanged quantitatively within ca. 1 h when kept in deuterium oxide containing catalytic amounts of potassium carbonate. This enhanced acidity may be due to inductive stabilization of the carbanion negative charge, located in an *sp*^{2}-orbital coplanar with the triazole ring, by the positive charge developed at N-1 and N-3 on *N*-oxidation. A similar stabilization accounts for the acidity of the ring protons of the corresponding triazolium salts.[7] In spite of the different nature of the *N*-substituents of the *N*-oxides, the ring protons are of similar acidity. Thus, the relative exchange rates of H-4 and H-5 are only 1.8:1 in 2, 2.4:1 in 3 and 6.1:1 in 4. Substituents such as halogen or a methoxy group activate adjacent protons. Deprotonation may be followed by electrophilic addition to the carbanion, a sequence of great preparative potential.

Scheme 5.

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Br
RN⁺N–O⁻ ⟶ RN⁺N–O⁻
N   N

19	2
12	3
21	4

Scheme 6.

1 h to give the triazole-1-oxides **2**, **3** and **4**, respectively, in virtually quantitative yield (Scheme 6). The facile debromination may be explained by bromonium ion abstraction, favoured since it leaves a stabilized carbanion (e.g. **48**).

Thus, 3-methyl-5-chlorotriazole-1-oxide (**18**) was deprotonated with sodium hydride in *N,N*-dimethylformamide (DMF) and the anion trapped with sulfur to give the 4-mercapto derivative **41** (Scheme 5). Electrophiles like dimethyl disulphide and methyl iodide also trapped the carbanion effectively (Scheme 5). In the former case the methanethiolate ion liberated by the methanethiolation displaces the chlorine of the initially formed 4-methylthio-5-chloro-substituted compound **42** to give **44**. The methanethiolate ion then demethylates **42** and **44**, producing as the final products the chloro-substituted mercaptotriazole-1-oxide **41** and a single methylthiomercaptotriazole-1-oxide assumed to be **43** since a methylthio group at C-4 is dealkylated more readily than one at C-5.[9] Realkylation of the mercaptotriazole-1-oxides **41** and **43** with methyl iodide took place exclusively at the sulfur atoms, affording the methylthio-substituted compounds **42** and **44**, respectively.

Deprotonation followed by electrophilic addition thus allows introduction of electrophiles at C-4 of 5-halogeno-substituted triazole-1-oxides, a position otherwise not susceptible to electrophilic attack in the parent 1-substituted triazoles.
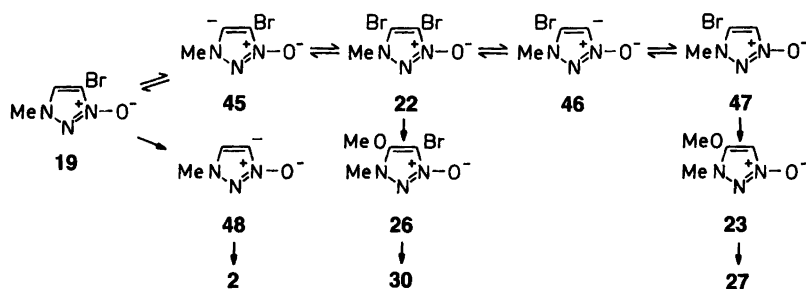
Debromination

The 5-bromotriazole-1-oxides **19**, **12** and **21** were debrominated by sodium sulfite at 100 °C within

Cine-substitution

Treatment of 3-methyl-5-chlorotriazole-1-oxide (**18**) with methanolic sodium methoxide at 140 °C for 5 h produced the 5-hydroxytriazole-1-oxide **35**, the initially formed 5-methoxy compound **33** being dealkylated under the reaction conditions. In contrast, the corresponding bromo compound **19** reacted with sodium methoxide at room temperature to give the *cine*-substitution product **23**, which dealkylates producing the hydroxy compound **27** (Scheme 7). Upon remethylation the latter compound gave **31** and **23**. The reason why *cine*-substitution of **19** takes place may be that the bromine is located at the less reactive position with respect to nucleophilic displacement. Therefore, it is not displaced by methoxide ions but is abstracted as a bromonium ion, since this creates a stabilized anion (**48**). The bromonium ion thus formed brominates the anion **45** derived from unchanged starting material. This gives rise to the dibromo compound **22** which may lose a bromonium ion to give the anion **46**. This on protonation produces in turn the bromo compound **47**. In the latter, the bromine is situated at the position reactive towards nucleophilic displacement, which leads to the methoxy compound **23**.

When the reaction was quenched with acid after 3 h the intermediate dibromo compound **22** could be isolated in 13 % yield. The mechanism is further confirmed by the observation of two byproducts. The first, 3-methyltriazole-1-oxide (**2**), is formed by protonation of the anion **48**. The latter is not susceptible to attack by bromonium

Me N⁺N–O⁻ ⇌ Me N⁺N–O⁻ ⇌ Me N⁺N–O⁻ ⇌ Me N⁺N–O⁻
N   N   N   N
45   22   46   47

Br
Me N⁺N–O⁻
N
19

Me N⁺N–O⁻   Me O Br   Me O
N   Me N⁺N–O⁻   Me N⁺N–O⁻
N   N   N
48   26   23

2   30   27

Scheme 7.

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ions under the conditions of the reactions, as indicated by a control experiment in which **2** remained unchanged upon treatment with sodium methoxide and *N*-bromoacetamide, an effective bromonium ion donor.[7] The second by-product is the hydroxy-substituted bromo compound **30**, remethylated to give **26** and **32**. The isolation of these compounds demonstrates the intermediacy of the dibromo compound **22**.

Experimental

The screw-cap-sealed reaction vessels used in some reactions are described in Ref. 10. Magnesium sulfate was used for drying, and solvents were removed under reduced pressure. Flash chromatography was performed as described in Ref. 11. All new compounds were colourless unless otherwise stated. The purity and identity of all compounds were confirmed using TLC and melting points, and by IR, ^{1}H NMR and mass spectra. ^{1}H NMR spectra (90 MHz) were recorded on a Bruker HX-90, and ^{13}C NMR spectra (22.63 MHz) on a Bruker WH-90 instrument. Mass spectra were obtained on a V. G. Micromass 7070 F instrument.

Preparation of 3-substituted triazole-1-oxides. (a) A mixture of 1-methyl-triazole (0.54 g),[6] *m*-chloroperoxybenzoic acid (1.40 g) and ethyl acetate (1.0 ml) was kept for 96 h at room temper-

ature and then heated under reflux for 10 min. Removal of the ethyl acetate, extraction with water (4×3 ml), passage of the solution through Amberlite IRA 400 (OH^--form) (2 ml) and removal of the water at 20 °C gave a residue which was washed with ether (3×3 ml), affording 0.45 g (71%) of 3-methyl-1,2,3-triazole-1-oxide (**2**), m.p. 123–124 °C. Purification: see Table 1. Spectral data: see Table 2.

(b) The 1-substituted triazole (1.0 g) was dissolved with heating in ethyl acetate (1ml). After cooling to 20 °C *m*-chloroperoxybenzoic acid (1.2 molar equiv.) was added. The mixture was stirred for 120 h, diluted with dichloromethane (10 ml) and washed with 1 M aqueous sodium hydroxide (8 ml). The aqueous solution was extracted with dichloromethane (2×8 ml). The combined organic phase was dried, the dichloromethane was removed, ethyl acetate (10 ml) was added, and the suspension was filtered through silica gel (Merck 60) (2 g). Washing with a further 2×10 ml of ethyl acetate and removal of the ethyl acetate gave unchanged starting material. Subsequent extraction of the silica gel with ethyl acetate/methanol (1:1) (5×10 ml) and removal of the solvents gave the crude 3-substituted 1,2,3-triazole-1-oxide. Yields and spectral data are given in Table 1.

(c) As in (b), replacing ethyl acetate with ether in the filtration through silica gel.

(d) As in (b), but filtration through silica gel

Table 1. Preparation of 3-substituted 1,2,3-triazole-1-oxides (**2–13**) from 1-substituted triazoles (**1**).

Compound	R	R'	R"	Starting material Ref.	Procedure	Yield/%	M.p./°C	Recovered starting material/%	Recrystal-lization medium[a]	M.p. of pure compound/°C[b]
2	Me	H	H	5	a	71	123–124	–	B	123–124
3	Bn	H	H	12	b	48	124	–	B	126–128
4	Ph	H	H	15	b	53	151–153	44	B	152–153
5	Ph	Me	H	18	b	74	127–128	25	A	128
6	Ph	Ph	H	17	b	47	185	27	B	199–200
7	Bn	Cl	H	4	b	31	70–71	63	A	96
8	Ph	Cl	H	19	d	26		62	D	85–87
9	Ph	H	Me	16	b	85	196–199	10	C	200
10	Ph	H	Ph	17	b	77	191–193	19	B	198
11	Bn	H	Cl	c	b	6	78–92	87	A	125
12	Bn	H	Br	13	b	17	129–133	79	B	134
13	Bn	H	OMe	14	c	19	Oil	77		–

[a]A, ethyl acetate; B, 2-propanol; C, methanol; D, ethyl acetate-hexane. [b]All compounds gave C,H and N elemental analyses which agreed to within ±0.3 % units with the calculated values. [c]See Experimental.

was replaced by flash chromatography using ethyl acetate as eluent. This gave unchanged starting material. Subsequent elution with acetone afforded the N-oxide.

(e) As in (b), but after removal of the dichloromethane the crude product was recrystallized from 2-propanol.

Preparation of 1-benzyloxytriazole. Benzylbromide (1.0 ml) was added with stirring at −10 °C to a mixture of 1-hydroxytriazole (0.65 g),[9] methanol (7.6 ml), and sodium hydroxide (0.38 g). The mixture was stirred at −10 °C for 0.5 h and at 20 °C for 3 d. Removal of the methanol, extraction with ether (3×10 ml) and removal of the ether gave an oil which was washed with boiling hexane (3×5 ml), cooling the mixture to −25 °C before decanting. The residue was dissolved in ethyl acetate (2 ml) and filtered through silica gel (2 g, 1 cm funnel), eluting with a further 4×5 ml of ethyl acetate. Removal of the ethyl acetate gave 0.51 g (38 %) of 1-benzyloxy-1,2,3-triazole (**14**), m.p. ca. 0 °C. Reprecipitation from ether/hexane gave an analytically pure specimen. Anal. $C_9H_9N_3O$: C,H,N. ^1H NMR (CDCl$_3$): δ 7.50 (1H, d, J 0.85 Hz, H-4), 7.25–7.45 (5H, m, Ph), 7.13 (1H, d, J 0.85 Hz, H-5), 5.41 (2H, s, CH$_2$); MS [m/e(% rel. int.)]: 175 (3, M), 91 (100).

Methylation of 3-substituted triazole-1-oxides. General procedure. The triazole-1-oxide (10 mmol) and trimethyloxonium tetrafluoroborate (10.8 mmol) were dissolved in liquid sulfur dioxide (ca. 7.5 ml). After reflux [condenser with dry ice and drying tube (containing calcium sulfate)] for 1 h the sulfur dioxide was allowed to evaporate. Recrystallization [dry methanol (ca. 2 ml)/ dry ether (ca. 30 ml)] gave the crude 1,2,3-triazolium tetrafluoroborate. In this way 3-methyltriazole-1-oxide (**2**) afforded 100 % of 1-methoxy-3-methyl-1,2,3-triazolium tetrafluoroborate (**15**), m.p. 48–50 °C (methanol/ether). Anal. $C_4H_8N_3OBF_4$: C,H,N. ^1H NMR (CDCl$_3$): δ 8.60 (1H, d, J 1.4 Hz, H-4), 8.33 (1H, d, J 1.4 Hz, H-5), 4.52 (3H, s, OMe), 4.38 (3H, s, sharpens on irradiation at 8.60, NMe).

Similarly, 3-benzyltriazole-1-oxide (**3**) gave 97 % of 1-methoxy-3-benzyl-1,2,3-triazolium tetrafluoroborate (**16**) as an oil. Anal. $C_{10}H_{12}N_3OBF_4$: C,H,N. ^1H NMR (CDCl$_3$): δ 8.53 (1H, d, J 1.6 Hz, sharpens on irradiation at 5.69, H-4), 8.44 (1H, d, J 1.6 Hz, H-5), 7.55–7.25 (5H, m, Ph), 5.69 (2H, s, CH$_2$), 4.43 (3H, s, Me).

Similarly, 3-phenyltriazole-1-oxide (**4**) gave 92 % of 1-methoxy-3-phenyl-1,2,3-triazolium tetrafluoroborate (**17**), m.p. 84–88 °C (methanol/ether). Anal. $C_9H_{10}N_3OBF_4$: C,H,N. ^1H NMR (CDCl$_3$): δ 8.91 (1H, d, J 1.6 Hz, H-4), 8.67 (1H, d, J 1.6 Hz, H-5), 7.95–7.4 (5H, m, Ph), 4.63 (3H, s, Me).

Chlorination of 3-substituted triazole-1-oxides. (a) 15 % Aqueous sodium hypochlorite (17.5 ml) was added dropwise with stirring and cooling in an ice bath to a solution of 3-methyltriazole-1-oxide (**2**) (0.99 g) in 4 M hydrochloric acid (13.8 ml) over a period of 10 min. After stirring at 20 °C for 5 h the mixture was evaporated to dryness. Extraction with boiling pyridine (3×10 ml) and removal of the pyridine gave 1.13 g (84 %) of 3-methyl-5-chloro-1,2,3-triazole-1-oxide (**18**), m.p. 170 °C. Recrystallization (2-propanol) gave m.p. 187–188 °C. Analytical data are given in Table 2. X-ray crystallographic analysis: see Ref. 2.

(b) 15 % aqueous sodium hypochlorite (17.5 ml) was added dropwise with stirring and cooling in an ice bath to a mixture of 3-benzyltriazole-1-oxide (**3**) (1.75 g), 4 M hydrochloric acid (13.8 ml) and chloroform (25 ml) over a period of 10 min. After stirring at 20 °C for 1.5 h sodium sulfite (3 g) was added. The organic phase was isolated. The aqueous solution was extracted with dichloromethane (2×30 ml). The organic phases were combined. Drying, removal of the solvents, extraction with boiling methanol (3×10 ml), filtration through activated carbon, and removal of the methanol gave a residue which was dissolved in boiling ethyl acetate (17 ml per g). The hot solution was pressure-filtrated through silica gel (1.8 g per g, diameter of funnel 2.5 cm). The silica gel was extracted further five times with boiling ethyl acetate (1.7 ml per g). Removal of the ethyl acetate gave a product free of starting material [TLC, acetone/ hexane (1:1)]. Recrystallization (ethyl acetate, 7.8 ml per g) with cooling to −25 °C gave 1.76 g (84 %) of 3-benzyl-5-chlorotriazole-1-oxide (**11**), identical with the material described in Table 1.

(c) Similarly, using 23.5 ml of hypochlorite solution, 18.5 ml of 4 M hydrochloric acid and 8 h reaction time, 3-phenyltriazole-1-oxide (**4**) (1.61 g) gave, after removal of the methanol, a product free of starting material which was re-

crystallized from ethyl acetate (10 ml per g) affording 1.62 g (83 %) of 3-phenyl-5-chloro-1,2,3-triazole-1-oxide (20), m.p. 148–150 °C. Analytical data are given in Table 2.

Bromination of 3-substituted triazole-1-oxides. (a) Bromine (2.5 ml) was added over a period of 5 min with stirring and cooling at 0 °C to a mixture of 3-methyltriazole-1-oxide (2) (1.22 g), chloroform (15 ml), sodium carbonate (2.6 g) and water (20 ml). Stirring was continued at 20 °C for 3 h. Neutralization to pH ca. 7 (hydrochloric acid), evaporation to dryness, extraction with boiling pyridine (4×20 ml) and removal of the pyridine gave 2.17 g (98 %) of 3-methyl-5-bromo-1,2,3-triazole-1-oxide (19), m.p. 195–196 °C. Recrystallization (2-propanol) gave m.p. 204 °C. Analytical data are given in Table 2.

(b) As in (a), using 3-benzyltriazole-1-oxide (3) (2.19 g). After removal of the chloroform, sodium sulfite (1 g) was added. Extraction with dichloromethane (3×10 ml), drying, removal of the dichloromethane, extraction with boiling methanol (3×10 ml), filtration through activated carbon and removal of the methanol gave 2.48 g (78 %) of 3-benzyl-5-bromotriazole-1-oxide (12), identical with the material described in Table 1.

Similarly, 3-phenyltriazole-1-oxide (4) afforded 78 % of 3-phenyl-5-bromo-1,2,3-triazole-1-oxide (21), m.p. 145–148 °C. Recrystallization (Methanol/ether) raised the m.p. to 150–152 °C. Analytical data are given in Table 2.

(c) 3-Benzyltriazole-1-oxide (3) (1.00 g), potassium carbonate (1.14 g), chloroform (10 ml) and bromine (0.48 ml) were stirred until TLC [2-butanone/water (10:1)] indicated that all starting material had been consumed (ca. 72 h). Filtration, extraction with dichloromethane (2×5 ml) and removal of the solvents gave 1.45 g (100 %) of 3-benzyl-5-bromotriazole-1-oxide (12), identical with the material described in Table 1.

Nitration of 3-phenyltriazole-1-oxide. A mixture of 3-Phenyltriazole-1-oxide (4) (0.30 g) and fuming nitric acid (d 1.55 g ml^{-1}) (1.85 ml) was kept at 20 °C for 1 h. Dilution with water (18.5 ml), filtration, and washing with water (3×2 ml) gave 0.34 g (89 %) of 3-p-nitrophenyl-1,2,3-triazole-1-oxide (2: R=p-NO$_2$C$_6$H$_4$, R'=R''=H), m.p. 258 °C. Recrystallization (acetonitrile) did

not raise the m.p. Anal. C$_8$H$_6$N$_4$O$_3$: C,H,N. ^{1}H NMR (DMSO-d_6): δ 9.21 (1H, d, J 1.7 Hz, H-4), 8.08 and 8.44 (4H, AA'XX', C$_6$H$_4$), 8.03 (1H, d, J 1.7 Hz, H-5).

Reaction of halogeno-substituted triazole-1-oxides with sodium methoxide. (a) 3-Benzyl-4-chlorotriazole-1-oxide (7) (0.24 g) and 1 M sodium methoxide in methanol (3.6 ml) were stirred together at 20 °C for 6 d. Removal of the methanol, addition of water (5 ml), extraction with dichloromethane (3×5 ml), drying and removal of the dichloromethane gave 0.20 g (88 %) of 3-benzyl-4-methoxy-1,2,3-triazole-1-oxide (24), m.p. 108–110 °C. Recrystallization (ethyl acetate) gave m.p. 112–114 °C. Analytical data are given in Table 2.

(b) The same reaction was performed by heating to 100 °C for 3 h in a screw-cap-sealed reaction vessel. The methanol was removed and water (3.7 ml) was added. Acidification (hydrochloric acid), filtration, and washing with water and dichloromethane gave 0.22 g (98 %) of 3-benzyl-4-hydroxy-1,2,3-triazole-1-oxide (28), m.p. 165–168 °C. Recrystallization from pyridine/ethyl acetate gave m.p. 168–169 °C. Analytical data are given in Table 2.

(c) As in (a), after 5 d 3-phenyl-4-chlorotriazole-1-oxide (8) afforded 71% of 3-phenyl-4-methoxy-1,2,3-triazole-1-oxide (25), m.p. 112–114 °C. Recrystallization (ethyl acetate/hexane) gave m.p. 118 °C. Analytical data are given in Table 2.

(d) 3-Phenyl-4-chlorotriazole-1-oxide (8) (0.25 g) and 1 M sodium methoxide in methanol (4.1 ml) were heated together to 100 °C for 3 h in a screw-cap-sealed reaction vessel. Removal of the methanol, addition of water (5 ml), washing with dichloromethane (2×5 ml), heating to 70 °C, acidification to pH 3 (hydrochloric acid), extraction with dichloromethane (3×5 ml), drying, and removal of the dichloromethane left 0.13 g (71 %) of 3-phenyl-4-hydroxy-1,2,3-triazole-1-oxide (29), m.p. 124–128 °C. Recrystallization (chloroform/ethyl acetate) gave m.p. 132–133 °C. Analytical data are given in Table 2.

(e) 3-Methyl-5-chlorotriazole-1-oxide (18) (0.33 g) and 1 M sodium methoxide in methanol (8.0 ml) were heated together to 140 °C for 5 h in a screw-cap-sealed reaction vessel. 1 M hydrochloric acid was added to give pH 2 (ca. 3.7 ml). The mixture was evaporated to dryness and ex-

Table 2. ^{1}H NMR^a and mass spectrometric data of 3-substituted 1,2,3-triazole-1-oxides.

Compound^b	R	R'	R"	H-4	H-5	Ph	CH$_2$	OMe	NMe	SMe	CMe	MS^c
2	Me	H	H	7.57^{d,e}	7.31				3.93			^{j}
3	Bn	H	H	7.53^{d,f}	7.27	7.2–7.45	5.26					^{k}
4	Ph	H	H	7.93^g	7.48	7.35–7.7						^{l}
5	Ph	Me	H		7.30	7.35–7.6					2.35	
6	Ph	Ph	H		7.50	7.1–7.5						
7	Bn	Cl	H		7.32	7.44	5.29					
8	Ph	Cl	H		7.49	7.54						
27	Me	OH	H^h		5.84				3.20			^{m}
28	Bn	OH	H^b		6.90	7.45–7.15	5.10					^{n}
29	Ph	OH	H		7.00	7.6–7.8 7.25–7.55						^{o}
23	Me	OMe	H		6.87			3.83	3.64			^{p}
24	Bn	OMe	H		6.93	7.3	5.09	3.93				^{q}
25	Ph	OMe	H		7.08	7.3–7.7		4.03				^{r}
9	Ph	H	Me	7.91		7.3–7.5						
10	Ph	H	Ph	7.53		7.1–7.5						
18	Me	H	Cl	7.52					3.93			^{s}
11	Bn	H	Cl	7.60		7.15–7.45	5.26					
20	Ph	H	Cl	8.02		7.4–7.65						
19	Me	H	Br	7.63^c					3.96			^{t}
12	Bn	H	Br	7.69		7.34	5.29					
21	Ph	H	Br	8.22		7.35–7.7						
35	Me	H	OH^h	7.17					3.81			^{u}
36	Bn	H	OH^h	7.40		7.36	5.29					^{v}
37	Ph	H	OH^h	8.30		7.9–7.4						^{x}
33	Me	H	OMe	7.34				4.00	3.88			^{y}
13	Bn	H	OMe	7.10		7.15–7.5	5.20	3.95				
40	Me	Me	Cl						3.86		2.35	
22	Me	Br	Br						3.95			^{z}
26	Me	OMe	Br					4.23	3.70			
41	Me	SH	Cl^i						3.61			
42	Me	SMe	Cl						3.98	2.49		
43	Me	SH	SMe^i						3.63	2.23		
44	Me	SMe	SMe						3.96	2.54 2.48		

^{a}Chemical shifts in deuteriochloroform solution (in ppm relative to tetramethylsilane) unless otherwise stated.
^{b}For notation, cf. structure **1** (Scheme 1). All compounds gave C,H and N elemental analyses which agreed to within ±0.3 % units with the calculated values with the following exceptions: The analytical data for **41** agreed with its monohydrate. The composition of compounds **22, 27** and **33** was only checked by high resolution mass spectrometry. ^{c}m/z (% rel. int.). ^{d}H-4 was assigned as the signal broadened by $^4J_{HCNCH_x}$-coupling disappearing upon irradiation of the NCH$_x$-group. $^eJ_{H-4,H-5} = 1.35$ Hz. $^fJ_{H-4,H-5} = 1.35$ Hz. $^gJ_{H-4,H-5} = 1.3$ Hz. ^{h}In DMSO-d_6. ^{i}In CD$_3$CN. ^{j}99 (100, *M*), 83 (5, *M*−0). ^{k}175 (1, *M*), 159 (3, *M*−0), 91 (100). ^{l}161 (19, *M*), 145 (12, *M*−0), 77 (100). ^{m}115.041 (35) (C$_3$H$_5$N$_3$O$_2$ requires 115.038). ^{n}191 (8, *M*), 91 (100). ^{o}177 (25, *M*), 161 (1, *M*−0), 77 (100). ^{p}129 (100, *M*), 113 (1, *M*−0). ^{q}205 (4, *M*), 91 (100). ^{r}191 (66, *M*), 175 (1,*M*−0), 77 (100). ^{s}135 (35, *M*+2), 133 (100, *M*), 117 (2, *M*−0). ^{t}179 (96, *M*+2), 177 (97, *M*), 161 (1, *M*−0), 43 (100). ^{u}115 (21, *M*), 99 (18, *M*−0), 42 (100). ^{v}191 (4, *M*), 175 (5, *M*−0), 91 (100). ^{x}177 (6, *M*), 161 (9, *M*−0), 77 (100). ^{y}129.054 (60) (C$_4$H$_7$N$_3$O$_2$ requires 129.054), 128 (53, *M*−H), 113 (7, *M*−0), 43 (100). ^{z}254.863 (14, pattern characteristic of 2 Br) (C$_3$H$_3$N$_3$OBr$_2$ requires 254.864).

tracted with boiling pyridine (3×3 ml). The extract was kept at 20 °C for 1 h, filtered, and the pyridine removed. To the residue was added dichloromethane (5 ml). After 1 h, during which separation took place, the mixture was filtered. The residue was washed with dichloromethane (2×5 ml) to yield 0.13 g (92 %) of cream-coloured 3-methyl-5-hydroxy-1,2,3-triazole-1-oxide (**35**), m.p. 184 °C (decomp.). Analytical data are given in Table 2.

(f) Using the reaction conditions in (e) and the work-up conditions in (b), 3-benzyl-5-chlorotriazole-1-oxide (**11**) produced 100 % of 3-benzyl-5-hydroxy-1,2,3-triazole-1-oxide (**36**), m.p. 132–133 °C. Recrystallization (acetonitrile) did not raise the m.p. Analytical data are given in Table 2.

(g) As in (f), 3-phenyl-5-chlorotriazole-1-oxide (**20**) afforded 78 % of 3-phenyl-5-hydroxy-1,2,3-triazole-1-oxide (**37**), m.p. 190 °C (decomp.). Recrystallization (acetonitrile) did not raise the m.p. Analytical data are given in Table 2.

(h) 3-Methyl-4,5-dibromotriazole-1-oxide (**22**) (0.10 g) and 1 M sodium methoxide in methanol were stirred together at 20 °C for 6 d in a screw-cap-sealed reaction vessel. Addition of methyl iodide (0.21 ml), stirring at 60 °C for 3 h, removal of the methanol, extraction with boiling dichloromethane (3×10 ml), removal of the dichloromethane, and preparative TLC (acetone) gave 9 mg (11 %) of *anhydro*-1-methoxy-3-methyl-4-hydroxy-5-bromotriazolium hydroxide (**32**) (R_F 0.44) m.p. 108–109 °C (ethyl acetate). Anal. $C_4H_6N_3O_2Br$: C,H,N. ¹H NMR (CDCl₃): δ 4.46 (3H, s, OMe), 4.02 (3H, s, NMe). The second fraction contained 18 mg (22 %) of 3-methyl-4-methoxy-5-bromotriazole-1-oxide (**26**) (R_F 0.28), m.p. 155–156 °C (2-propanol). Analytical data are given in Table 2.

Demethylation of methoxytriazole-1-oxides. (a) 3-Methyl-4-methoxytriazole-1-oxide (**23**) (69 mg) and 1.25 M lithium methoxide in methanol (0.94 ml) were heated together in a screw-cap-sealed reaction vessel to 100 °C for 3 h. Addition of hydrochloric acid to give pH 6, removal of the solvents, and washing with boiling pyridine (3×2 ml) afforded 51 mg (82 %) of 3-methyl-4-hydroxy-1,2,3-triazole-1-oxide (**27**), m.p. 242–244 °C (decomp.). Recrystallization (methanol/ether) did not raise the m.p. ¹H NMR and MS

data are given in Table 2. ¹³C NMR [D₂O+H₂O (1:1)]: δ 156.6 (s, C-4), 102.4 (d, $^1J_{CH}$ 203.1 Hz, C-5), 31.1 (q, $^1J_{CH}$ 141.9 Hz, NMe).

(b) Similarly, *anhydro*-1-methoxy-3-methyl-4-hydroxytriazolium hydroxide (**31**) (37 mg) produced 35 mg of **27** containing minor impurities (¹H NMR).

Methylation of hydroxy-substituted triazole-1-oxides. (a) 3-Methyl-4-hydroxytriazole-1-oxide (**27**) (0.20 g), 1 M sodium methoxide in methanol (2.35 ml), and methyl iodide (0.23 ml) were heated together in a screw-cap-sealed reaction vessel to 60 °C for 3 h. Removal of the methanol, extraction with dichloromethane (3×10 ml), removal of the dichloromethane, and preparative TLC [2-butanone/water (10:1)] gave 191 mg (85 %) of *anhydro*-1-methoxy-3-methyl-4-hydroxy-1,2,3-triazolium hydroxide (**31**) (R_F 0.20) as a semicrystalline mass which was reprecipitated from ethyl acetate/hexane. The compound is very hydroscopic and a correct analysis could not be obtained. Found: C 36.1; H 5.7; N 30.85. Calc. for $C_4H_7N_3O_2$: C 37.2; H 5.45; N 32.55. ¹H NMR (CDCl₃): δ 6.60 (1H, s, H-5), 4.22 (3H, s, OMe), 3.66 (3H, s, NMe). MS [*m/z* rel. int.)]: 129 (75, *M*), 113 (6, *M*−O), 86 (78), 43 (100). IR in KBr disc: 1653 cm⁻¹. The next fraction contained 13 mg (6 %) of 3-methyl-4-methoxytriazole-1-oxide (**23**) (R_F 0.13), identical with the material described below.

(b) Similarly, 3-methyl-5-hydroxytriazole-1-oxide (**35**) gave a crude product which on preparative TLC [2-butanone/water (10:1)] gave 0.24 g (93 %) of *anhydro*-1-methoxy-3-methyl-5-hydroxy-1,2,3-triazolium hydroxide (**38**) (R_F 0.17) as deliquescent crystals. Recrystallization (ethyl acetate/hexane) gave m.p. 68–70 °C. The compound is very hygroscopic and a correct analysis could not be obtained. Found: C 36.75; H 6.3; N 31.65. Calc. for $C_4H_7N_3O_2$: C 37.2; H 5.45; N 32.55. ¹H NMR (CDCl₃): 6.59 (1H, s, H-4), 4.17 (3H, s, OMe), 3.87 (3H, s, NMe). MS [*m/z* (% rel. int.)]: 129 (89, *M*), 42 (100). IR in KBr disc: 1644 cm⁻¹. The second fraction contained 21 mg (7 %) of 3-methyl-5-methoxy-1,2,3-triazole-1-oxide (**33**) (R_F 0.08) as a semicrystalline mass which was reprecipitated from ethyl acetate/hexane. NMR and MS data are given in Table 2.

Debromination. 3-Methyl-5-bromotriazole-1-ox-ide (**19**) (0.56 g), sodium sulfite (1.19 g) and wa-ter (5.6 ml) were heated under reflux for 1 h. The water was removed and the residue was ex-tracted with boiling acetonitrile (3×10 ml). Re-moval of the acetonitrile afforded 3-methyltria-zole-1-oxide (**2**), identical with the material above, in quantitative yield.

Similarly, 3-benzyl-5-bromotriazole-1-oxide (**12**) produced 3-benzyltriazole-1-oxide (**3**) (98%), and 3-phenyl-5-bromotriazole-1-oxide (**21**) gave 3-phenyltriazole-1-oxide (**4**) (97%).

Deprotonation of 3-substituted triazole-1-oxides followed by electrophilic addition. (a) Under ni-trogen, a 55% suspension of sodium hydride in mineral oil (0.25 g) was washed with dry hexane. 3-Methyl-5-chlorotriazole-1-oxide (**18**) (0.41 g) and sulfur (0.78 g) were added. Dry DMF (3.2 ml) was added at −78°C. After stirring at 0°C for 3 h and at 20°C for 24 h the DMF was removed at 40°C/1 mmHg. Addition of water, acidification to pH 4 (hydrochloric acid), filtra-tion, removal of the water, extraction with boil-ing pyridine (3×5 ml), removal of the pyridine, and washing with carbon disulfide (2×5 ml) and dichloromethane (2×5 ml) produced 0.51 g (100%) of 3-methyl-4-mercapto-5-chloro-1,2,3-triazole-1-oxide (**41**), m.p. 198–202°C. Recrystal-lization (2-propanol) gave m.p. 216–218°C (de-comp.). Analytical data are given in Table 2.

Methylation as described for 3-methyl-4-hy-droxytriazole-1-oxide (**27**) gave a dichlorometh-ane solution containing 94% of cream-coloured 3-methyl-4-methylthio-5-chloro-1,2,3-triazole-1-oxide (**42**), m.p. 91–92°C (ethyl acetate). Analyt-ical data are given in Table 2.

(b) Replacing the sulfur with dimethyl disul-fide (1.09 ml) and extending the reaction time to 72 h, after removal of the DMF, addition of wa-ter, washing with dichloromethane (2×5 ml), acidification to pH 4.5 (hydrochloric acid), re-moval of the water, extraction with acetonitrile (3×5 ml), and removal of the acetonitrile gave 0.47 g of a 1:1 mixture of 3-methyl-4-mer-capto-5-chlorotriazole-1-oxide (**41**), identical with the material described above, and 3-methyl-4-mercapto-5-methylthiotriazole-1-ox-ide (**43**). NMR data are given in Table 2. This mixture was methylated as described above for 3-methtyl-4-hydroxytriazole-1-oxide (**27**). Re-moval of the dichloromethane gave a residue

which was purified by preparative TLC [2-buta-none/water (10:1)] to give 40% of 3-methyl-4-methylthio-5-chlorotriazole-1-oxide (**42**) (R_F 0.48), identical with the material de-scribed above, and 50% of 3-methyl-4,5-bis (methylthio)-1,2,3-triazole-1-oxide (**44**) (R_F 0.38), a yellow oil. Reprecipitation (ethyl ace-tate/hexane) gave m.p. 65–68°C. Analytical data are given in Table 2.

(c) Performing the reaction as in (a), replacing sulfur with methyl iodide (0.75 ml), after remov-al of the DMF, addition of water (5 ml), extrac-tion with dichloromethane (3×5 ml), drying, and removal of the dichloromethane, afforded 89% of 3,4-dimethyl-5-chloro-1,2,3-triazole-1-oxide (**40**). Recrystallization (ethyl acetate) gave m.p. 151–157°C. Analytical data are given in Table 2.

Reaction of 3-methyl-5-bromotriazole-1-oxide with sodium methoxide. (a) 3-Methyl-5-bromo-triazole-1-oxide (**19**) (0.17 g) and 1 M sodium methoxide in methanol (3.0 ml) were mixed and kept for 7 d in a screw-cap-sealed reaction vessel. Methyl iodide (0.25 ml) was added and the mix-ture was heated to 60°C for 3 h. Evaporation to dryness, extraction with boiling dichloromethane (3×10 ml), removal of the dichloromethane, and preparative TLC [2-butanone/water (10:1)] gave 20 mg (10%) of *anhydro*-1-methoxy-3-methyl-4-hydroxy-5-bromotriazolium hydroxide (**32**) (R_F 0.48), 4 mg (2%) of 3-methyl-4-meth-oxy-5-bromotriazole-1-oxide (**26**) (R_F 0.42), 26 mg (15%) of unchanged starting material (R_F 0.39) and 16 mg (13%) of *anhydro*-1-meth-oxy-3-methyl-4-hydroxytriazolium hydroxide (**31**) (R_F 0.24), all identical with the compounds described above. The next fraction contained 46 mg (48%) of 3-methyl-4-methoxy-1,2,3-tria-zole-1-oxide (**23**) (R_F 0.11), m.p. 135–138°C. Re-crystallization (ethyl acetate/hexane) did not raise the m.p. Analytical data are given in Table 2. The last fraction contained 9 mg (10%) of 3-methyltriazole-1-oxide (**2**) (R_F 0.10), identical with the material described above.

(b) The reaction was performed as in (a) but quenched after 3 h by addition of 1 M hydro-chloric acid (3.9 ml). Removal of the water, extraction with boiling dichloromethane (3×10 ml), removal of the dichloromethane, and preparative TLC [2-butanone/water (10:1)] gave, in addition to other compounds, 31 mg (13%) of 3-methyl-4,5-dibromo-1,2,3-triazole-1-oxide (**22**)

Table 3. Deoxygenation of 3-substituted triazole-1-oxides **3**, **20** and **21** to 1-substituted triazoles (**1**).

Starting material	Product **1**			Yield/%	M.p./°C	Recrystallization medium	M.p. of pure compound/°C
	R	R′	R″				
3	Bn	H	H	86	57–59	Ether	61[a]
20	Ph	H	Cl	90	81–83	Ligroin	84–87[b]
21	Ph	H	Br	97	114–117	Ligroin	120–122[c]

[a]Reported[12] m.p. 61 °C. [b]Anal. $C_8H_6N_3Cl$: C,H,N. ^{1}HNMR (CDCl3): δ 8.01 (1H, s, H-5), 7.9–7.35 (5H, m, Ph).
[c]Reported[21] m.p. 122–123 °C.

(R_F 0.58), m.p. 235 °C (decomp.). NMR and MS data are given in Table 2.

Deoxygenation of 3-substituted triazole-1-oxides.
The triazole-1-oxide (0.1 mol) and phosphorus trichloride (0.22 mol) were stirred together and the mixture was heated under reflux for 1 h. Subsequent stirring with water (200 ml) for 1 h, extraction with dichloromethane (3×140 ml), drying (potassium carbonate), removal of the dichloromethane, dissolution in ether, filtration through activated carbon and removal of the ether left the crude triazole. Yields and recrystallization media are given in Table 3.

References

1. Hubert, A. J. *Bull. Soc. Chim. Belg. 79* (1970) 195.
2. Søtofte, I. *Acta Chem. Scand., Ser. B. In press.*
3. Begtrup, M. and Nytoft, H. P. *Acta Chem. Scand., Ser. B 40* (1986) 202.
4. Begtrup, M. and Holm, J. *J. Chem. Soc., Perkin Trans. 1* (1981) 503.
5. Begtrup, M. and Pedersen, C. *Acta Chem. Scand. 21* (1967) 633.
6. Pedersen, C. *Acta Chem. Scand. 13* (1959) 888.
7. Begtrup, M. *Acta Chem. Scand. 25* (1971) 803.
8. Raap, R. *Can. J. Chem. 49* (1971) 1792.
9. Begtrup, M. *To be published.*
10. Begtrup, M. *J. Chem. Educ.* (1987). *In press.*
11. Still, W. C., Kahn, M. and Mitra, A. *J. Org. Chem. 43* (1978) 2923.
12. Kelly, T. R., Dali, H. M. and Tsang, W.-G. *Tetrahedron Lett. 1977* 3859.
13. Wiley, R. H., Hussung, K. F. and Moffat, J. *J. Org. Chem. 21* (1956) 190.
14. Begtrup, M. *Acta Chem. Scand. 25* (1971) 249.
15. Begtrup, M. and Pedersen, C. *Acta Chem. Scand. 23* (1969) 1091.
16. Bertho, A. *Ber. Dtsch. Chem. Ges. 58* (1925) 859.
17. Munk, M. E. and Kim, Y. K. *J. Am. Chem. Soc. 86* (1964) 2217.
18. Kirmse, W. and Horner, L. *Ann. 614* (1958) 1.
19. Dimroth, O. *Ber. Dtsch. Chem. Ges. 35* (1902) 1029.
20. Lieber, E., Chao, T. S. and Ramachandra Rao, C. N. *J. Org. Chem. 22* (1957) 654.
21. Rondesvedt, C. S., Jr. and Chang, P. K. *J. Am. Chem. Soc. 77* (1955) 6532.

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